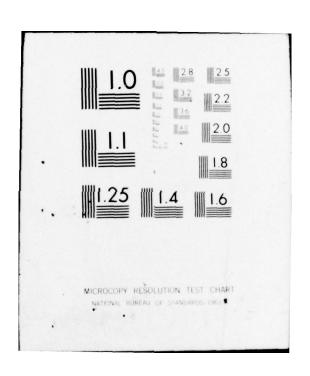AD-A037 105   GEORGETOWN UNIV WASHINGTON D C
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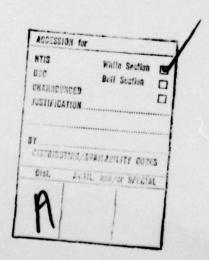|	
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Liquid crystals	Solvents
Phase transformations	Mixtures
Statistical mechanics	Binary systems (materials)

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This is a brief summary of the liquid crystal research supported by ARO at Georgetown University during the past ten years. Research has been directed toward a more detailed understanding, on a molecular level, of the thermodynamic properties of (a) phase transitions in liquid crystals and (b) binary mixtures of nonmesomorphic solutes and nematic (or cholesteric) solvents.

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8. **SCIENTIFIC PERSONNEL SUPPORTED (6 MONTHS OR MORE) BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:**

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   (f) Laurence C. Chow, Graduate Student (Ph.D., June 1970)
   (g) Joel M. Schnur, Graduate STudent (Ph.D., January 1972)
   (h) Henry T. Peterson, Graduate Student (Ph.D., with distinction, January 1973)
   (i) Gwo-Chung Lin, Graduate Student (Ph.D., June 1975)
   (j) Ghassan A. Oweimreen (Ph.D. expected June 1977)

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Daniel E. Martire
January 14, 1977

SUMMARY OF RESEARCH

The liquid crystal research supported by ARO at Georgetown University during these past ten years has been directed toward a more detailed understanding, on a molecular level, of the thermodynamic properties of (a) phase transitions in liquid crystals and (b) binary mixtures of nonmesomorphic solutes and nematic (or cholesteric) solvents.

The potential of gas-liquid chromatography (glc) for studying the thermodynamics of <u>infinitely</u> <u>dilute</u> solutions of nonmesomorphic solutes in liquid-crystalline solvents was demonstrated in an exploratory investigation (1). Subsequent experimental studies confirmed the validity of our glc approach by establishing the absence of surface effects (3,10) and the agreement between glc data and extrapolated static measurements (11). The glc method and a statistical-thermodynamic model were then successfully employed in obtaining and interpreting thermodynamic solution quantities for a wide range of solutes in nematic and cholesteric solvents (8,13,15,22). Our understanding of the unique solvent properties of liquid crystals has been advanced through these studies. Other novel applications of glc were developed: analytical separation of geometric isomers using a nematic liquid phase (4); determination of nematic order parameters by a solute probe method (9); and complementary thermodynamic studies to interpret the effect of organic solutes on the selective reflectance of visible light by cholesteric mixtures (12). Apparatus were designed and tested (11,20) for the thermodynamic study of mixtures of nonmesopmorphic solutes at <u>finite</u> <u>concentration</u> in nematic solvents. Experiments were conducted to investigate the effect of solute size, shape and flexibility on nematic phase stability (14,20).

Several statistical-mechanical models were developed to provide the necessary framework for interpreting the thermodynamic properties of liquid-crystalline phase transitions in one and two component systems. A scaled-particle theory (5,6,7) of rigid rods (one component) demonstrated the primary role of repulsive forces (or packing effects) in the nematic-isotropic liquid transition. A lattice model (2) of rigid rods was used to investigate the secondary effect of attractive forces. The results of both models suggested the probable importance of end-chain flexibility in homologous series. Accordingly, a rotational-isomeric model (15) and a lattice model of particles consisting of rigid central cores and semiflexible pendant groups (17) were developed to investigate the effect of end-chain flexibility. The results of these models (and available thermodynamic data) strongly indicated that the nematic-isotropic transition can be adequately described in terms of molecular packing and flexibility effects, with attractive forces providing a uniform background and having only a minor effect on the transition properties. A simple tunnel model of rigid rods (one component) was developed and successfully applied to interpret the thermodynamic behavior of the smectic A - nematic phase transition (21). Finally, models involving two components - mixtures of rigid rods of different lengths (16) and mixtures of rigid rods and spheres (18,19,20) - were developed to aid in interpreting the experimental results (14,20) for solute-induced nematic-isotropic phase transitions.

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1. Thermodynamics of Solutions with Liquid Crystal Solvents. I. A GLC Study of Cholesteryl Myristate, <u>Journal of Physical Chemistry</u>, <u>72</u>, 3489 (1968). (with P.A. Blasco, P.F. Carone, L.C. Chow and H. Vicini).

2. A Quasi-Chemical Lattice Treatment of Rod-like Molecules. Application to the Nematic-Isotropic Transition in Liquid Crystals, <u>Molecular Crystals and Liquid Crystals</u>, <u>7</u>, 295 (1969). (with M.A. Cotter).

3. Thermodynamics of Solutions with Liquid Crystal Solvents. II. Surface Effects with Nematogenic Compounds, <u>Journal of Physical Chemistry</u>, <u>73</u>, 1127 (1969). (with L.C. Chow).

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21. A Tunnel Model for the Nematic to Smectic A Transition in Liquid Crystals, Journal of Chemical Physics, in preparation. (with G.C. Lin and L.C. Chow).

22. Thermodynamics of Solutions with Liquid Crystal Solvents. IX. Non-mesomorphic Solutes in Nematic and Isotropic MBBA, Journal of Physical Chemistry, in preparation. (with G.C. Lin and G.A. Oweimreen).

Note:

a. D.E. Martire is one of the authors of each of the above manuscripts.

b. Reprints of manuscripts number 21 and 22, which are largely based on G.C. Lin's doctoral dissertation (see following page for abstract), will be sent to ARO following publication of the papers.

Thermotropic Liquid Crystals: A Cell Model for the
Smectic A-Nematic Transition and A Thermodynamic
Investigation of Dilute Solutions in Nematic
and Isotropic MBBA
(Ph.D. Dissertation of Gwo-Chung Lin)

Abstract

In order to gain a better understanding of the fundamental
nature of the smectic A-nematic transition in liquid crystals,
a simple cell model is applied to a fluid of aligned, rigid,
cylinders in Part I. Particle motion is separated into com-
ponents parallel and perpendicular to the long axis of the mole-
cules. The partition functions are formulated by considering
the contribution from particles localized within their cells
and the contribution from positional disorder in the nematic
phase. The transition temperature is determined by equating
the Helmholtz free energies of the two phases, in the limit of
zero external pressure.

When realistic values for the dimensional and energetic para-
meters are used in the model calculations, reasonable values are
obtained for the transition temperature, absolute density and
configurational energy. It is found that: (a) the smectic A
phase becomes more favored (i.e., the transition temperature
increases) as the strength of segmental core-core interactions
and/or the length of the central core increases, (b) the transi-
tion enthalpy, entropy and fractional volume change decrease
with increasing terminal interactions (ϵ'), while the transition
temperature is virtually insensitive to ϵ'. The most significant
success of the model is its ability to produce the observed trends
in the transition temperature and entropy in homologous series.

In Part II, gas-liquid chromatography is used to obtain
infinite dilution activity coefficients and partial molar en-
thalpies and entropies of solution for 26 nonmesomorphic solutes
in both the nematic and isotropic phases of N-(p-methoxy-benzyl-
idene)-p-n-butylaniline (MBBA). The data are interpreted in the
light of Chow and Martire's, and Humphries, James and Luckhurst's
statistical thermodynamic solution models, and are compared with
results obtained for other nematogenic compounds.